Annotated Solution 2002 USNCO National Exam Part I

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1 Solutions

1. D. Tl commonly exhibits both +1 and +3 oxidization states since it can lose its $6p^1$ electron or its $6p^1$ and $6s^2$ electrons. $6s^2$ is less likely to lose due to the so called " $6s^2$ inert pair effect".

2. The best way to extinguish burning magnesium is to C. cover it with sand in order to cut the oxygen supply. Never use water to extinguish unknown fires since reactive metals such as magnesium react violently with water at high temperature, which further produces hydrogen gas and makes it even worse.

3. Amphoterism is when a substance has both basic and acidic properties. By reacting $Zn(OH)_2$ with H^+ and OH^- ions, it will demonstrate both properties. Therefore, the answer is B.

4. D. is incorrect. The only two elements that are liquid at room temperature is Bromine and Mercury.

5.

$$\frac{1178 \text{ g} \times .25 \text{ H}_2 \text{SO}_4}{1 \text{ L}} \times \frac{1 \text{ mol}}{98 \text{ g}} \implies \boxed{\text{B.}}$$

6. The pressure will be too high since the calculated pressure will also include water vapor, so will be the mol of gas based on the ideal gas law. Since molar mass is calculated with $\frac{\text{mass}}{\text{mol}}$ and the mol amount is higher than the actual value, the molar mass will be less. Thus, the answer is $\boxed{\text{C}}$

7. A. NaHSO₄ is known to have a very large $K_{\rm a}$.

8. Notice that 3 mols of HCl are needed for each mol of trona (2 for the carbonate and 1 for the bicarbonate). Therefore, a mol conversion gives $\frac{0.407}{226 \times .125} \times 3 = 0.0432 \text{ L} = \boxed{\text{A. } 43.2 \text{ mL}}$

9. $\frac{52.2}{12.0} = 4.35, \frac{3.7}{1.01} = 3.7, \frac{44.1}{35.5} = 1.24$. These match a 7 : 6 : 2 ratio so the answer is D. 7

10. Using the ideal gas law, there are $\frac{1 \times .150}{.0821 \times 273} = .0067$ mol CO₂. There are $\frac{.500}{71} = .0071$ mol KO₂. However, since twice the amout of KO₂ will be consumed, KO₂ is the limiting reactant. It will produce $.0071 \times \frac{3}{4} = .0053$ mol O₂ and with the ideal gas law that gives $\frac{.0053 \times .0821 \times 273}{1} =$ A. 118 mL

11. A solution will have higher boiling points and lower freezing points compared to the pure solvent, so the answer is D.4 Please refer to the colligative properties of solutions for more information.

12. The partial pressures of each gas is proportional to the amount of mols in the container.

Since lower molar mass will result in more mols, the ranking should be D. $P_{N_2O} < P_{N_2} < P_{NH_3}$

13. B. Solid and gas are the only states that can exist under the triple point.

14. Using ideal gas law, there will be $\frac{92.5 \times 5.00}{760 \times .0821 \times 323} \times 18.0 = .413$ g of water in gas form. That means there will be $1.00 - 0.413 = \boxed{C.\ 0.59 \text{ g}}$ of water in liquid state.

15. From Coulomb's law, the attraction is proportional to the charge of the ions and inversely proportional to the distance of the two adjacent cation and anion, which is the sum of their radii. C. MgO both maximizes the charge of the ions while minimizing the distance.

16. As the temperature of a gas decreases, the attractive forces between the molecules will be stronger, which reduces the collision of gas molecules on the wall, and further decreases the pressure. Changing the temperature will experience no deviation from mass or volume of the molecules themselves since they stay constant. Therefore, the answer is A. 1 only

17. The length of the phase change is related to the value of enthalpy of that phase change as the x-axis is the heat added and the temperature keeps constant during phase change process. Since the phase change is fusion, that corresponds to the B length of BC

18. Since a coffee-cup calorimeter is a constant pressure system, $A. q = \Delta H$ is correct. A bomb calorimeter is a constant volume system, $q = \Delta E$ as w = 0.

19. From the equation $-4500 = 6(-241.8) + \Delta H_f - 4(9.2)$, we get $\Delta H_f = D. -3012 \text{ kJ}$

20. From the third law of thermodynamics, $S^o = 0$ when the temperature approaches 0 K. Thus, the answer is C. I and II only

21. The amount of energy released is $100 \times 4.18 \times 3.0 = 1.25$ kJ. There were $0.0500 \times 0.10 = .0050$ mol of HCl involved in the reaction. Thus, the enthalpy per mol is $-\frac{1.25}{.0050} = \boxed{A. -2.5 \times 10^2 \text{ kJ}}$

22. From the equation $\Delta G = \Delta H - T\Delta S$, ΔH is the *y*-intercept of the graph and $-\Delta S$ is the slope. Since the *y*-intercept is positive and the slope is negative, we can conclude $\overline{A. \Delta H > 0, \Delta S > 0}$

23. At the boiling point, $\Delta G = 0 = \Delta H - T\Delta S \implies \Delta S = \frac{\Delta H}{T} = \boxed{\text{B. 93.8}}$

24. Applying $\Delta G^{\circ} = -RT \ln K$ gives K =D. 4.5 ×10⁻⁶

25. For a second order reaction, plotting C. $1/[\mathbf{X}]$ vs. time gives a straight line based on the integrated rate law.

26. Using the formula $\ln[X]_t - \ln[X]_0 = -kt$, we have $\ln(.30) = -5.0k \implies k = \boxed{B. 0.24 \text{ min}^{-1}}$

27. Using the formula

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$
$$\ln(30) = \frac{E_a}{8.314} \left(\frac{1}{298} - \frac{1}{348}\right)$$
$$E_a = \boxed{A. 58.6 \text{ kJ/mol}}$$

28. From the first to second trial we can see the reaction is first order in $[I^-]$. From the second to third trial we can see the reaction is zeroth order in $[BrO_3^-]$. From the first to third trial we can see the reaction is first order in $[H^+]$. Therefore, the rate law is $Rate = k[H^+][I^-]$,

and balancing the units on each side gives k the units of C. L/mol \cdot s

29. B. Step **2** is the rate-determining step since it would have a rate law of Rate=k[Cl][CHCl₃]=k[CHCl₃][Cl₂]^{1/2} if pre-equilibrium approximation is applied to the first step, which is a fast equilibrium prior to a slow step. You may refer to the annotation of question #29 in 2003 for more information.

30. The desired reaction is equivalent to the first reaction minus the second reaction. Therefore, the equilibrium constant is equivalent to the constant of the first divided by the second, which is $\frac{1.7 \times 10^{-2}}{5.9 \times 10^{-5}} = \boxed{D. 2.9 \times 10^2}$

31. Letting $x = [OH^-]$, we have $K_b = 1.0 \times 10^{-6} = \frac{x^2}{0.15} \implies x = .00039$. pH= 14 + log(x) = [C. 10.59]

32. The reaction rate levels off since D. The active sites of the catalyst are occupied

33. If x is the amount that dissociates, we have $K_a = 1.9 \times 10^{-4} = \frac{x^2}{0.10-x} \implies x = .0044$. The percentage that dissociated is $\frac{.0044}{0.10} = \boxed{\text{C. } 4.4\%}$

34. We have $K_a = 1.9 \times 10^{-4} = \frac{[\text{HCOO}^-]10^{-4.00}}{0.20} \implies [\text{HCOO}^-] = \boxed{\text{A. 0.38 M}}$

35. When titrating a weak base with a strong acid, the equivalence point will be in the acidic range, so the indicator should also be in the A. acidic range

36. Let x be the molar solubility. Then, we have $K_{\rm sp} = 4.0 \times 10^{-6} = 4x^3 \implies x = 10 \times 10^{-2}$

37. Oxygen will have an oxidization state of -2 and Chloride will have a state of -1. Therefore, we have the equation 6(W) + 6(-2) + 12(-1) = -2 which gives the average oxidization state on W to be C. 3.7

38. For each oxygen added, 2 electrons need to be removed. For each hydrogen removed, 1 electron needs to be removed. Since from toluene to benzene, 2 oxygen are added and 2 hydrogen are removed, a total of D. 6 electrons are removed.

39. Since the second reaction is reversed, we can add the first potential to the negative of the second to get $0.34 + 1.66 = \boxed{B. 2.00 \text{ V}}$

40. The value of n should be A. 6 since that is the number of electrons transferred in the reaction.

41. When adding half reactions with electrons that do not cancel out, we take the weighted average of the electric potentials weighted by the number of electrons. We multiply each potential by their weight and divide by the total weight to get $\frac{0.564+2(2.261)}{3} = \boxed{A.\ 1.695 \text{ V}}$. You may derive the equation above based on Hess's Law and $\Delta G^{\circ} = -nFE^{\circ}$.

42. The number of Faradays is equal to the mol of electrons needed. Each mol of $\operatorname{Cr}_2\operatorname{O}_7^{2-}$ requires 8 mol of electrons to get to 2 mols of Cr^{2+} . Thus the Faradays required is $0.150 \times 0.115 \times 8 = \boxed{\operatorname{C}. 0.138 \operatorname{F}}$

43. First ionization energies increase going up and right in the periodic table, and B. S.O.F matches that description.

44. [B. l] is associated with the shape of an orbital. For example, s is the shape of a sphere, p is a dumbbell, and so on.

45. Elements with the diagonal relationship (to the right and down) such as D. Li⁺ and Mg²⁺

will have similar properties since the effects of moving right and down oppose each other.

46. Fe³⁺ will have a A. d^5 configuration since it will lose its outer s electrons before the d electrons.

47. Magnesium isotopes that are too light will undergo D. positron emission which decreases the atomic number and stabilizes the nucleus.

48. Al_2O_3 and SiO_2 are both network structures. B. 2 only exists as individual molecules.

49. There are 4 pi bonds in the structure, 3 in the benzene ring and 1 in the C=O double bond. Thus the answer is D. 15 sigma, 4 pi. We can also confirm the sigma bond count by counting the total number of bonds (including the C–H bonds in the benzene ring not shown)

50. A. CO_3^{2-} and NO_3^{-} are isoelectronic, so they will have the same shape (trigonal planar)

51. Structure [B] has the negative formal charge on the most negative element, oxygen, so it contributes most to the overall structure.

52. According to molecular orbital theory, $D. O_2^+$ has the strongest bond with a bond order of 2.5. The other species listed add antibonding electrons, weakening the bond.

53. Cr^{3+} has a coordination number of $\overline{\operatorname{C. 6}}$, which means i will covalently bond to 6 other atoms. So the correct formula of the compound is $[\operatorname{Cr}(\operatorname{NH}_3)_4\operatorname{Cl}_2]^+\operatorname{Cl}^-$ with a chloride ionically bonded.

54. CH₃OH is an alcohol and has a carbon-oxygen bond order of 1. H₂CO is formaldehyde which has a bond order of 2. HCO_2^- has a bond order of 1.5 from resonance. Therefore, the arrangement should be C. H₂CO, HCO_2^- , H_2CO in order of increasing length.

55. B. is an alcohol being oxidized to an aldehyde as two hydrogen atoms are gone.

56. The difference between the choices is the number of hydrogen atoms. There are 2 shown connected to the nitrogen and 8 not shown connected to the benzene rings for a total of 10 hydrogen atoms. Therefore, its formula is $C. C_{16}H_{10}N_2O_2$

57. The carbon is connected to 1 pi bond, making it $|B. sp^2|$ hybridized.

58. Since aniline is a weak base, adding [A. 1 M HCl] will give it H⁺ and transform it into an ion of RNH₃⁺ (R=benzene ring here), increasing solubility.

59. Tertiary carbons react most rapidly since the formation of carbocation is the rate-determining step in a solvation process, which is a $S_N 1$ mechanism, and the carbon cation formed as intermediate will be stabilized by more electron donating hyperconjugation effect on the tertiary carbon.

60. Hemoglobin is a part of our red blood cells, which is known to contain B. Fe